

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number  
**WO 2004/054708 A3**

(51) International Patent Classification<sup>7</sup>: **B01J 20/10**,  
20/28, 20/32, B01D 53/40, 53/62, 53/047

[CA/CA]; 735 Lugate Court, Ottawa, Ontario K1J 8K8  
(CA).

(21) International Application Number:  
PCT/CA2003/001968

(74) Agent: **WHITE, Stephanie, R.**; Osler, Hoskin & Harcourt  
LLP, Suite 1500, 50 O'Connor Street, Ottawa, Ontario K1P  
6L2 (CA).

(22) International Filing Date:  
18 December 2003 (18.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/433,967 18 December 2002 (18.12.2002) US

(71) Applicant (for all designated States except US): **UNIVER-  
SITY OF OTTAWA** [CA/CA]; 550 Cumberland Avenue,  
Ottawa, Ontario K1N 6N5 (CA).

(72) Inventor; and

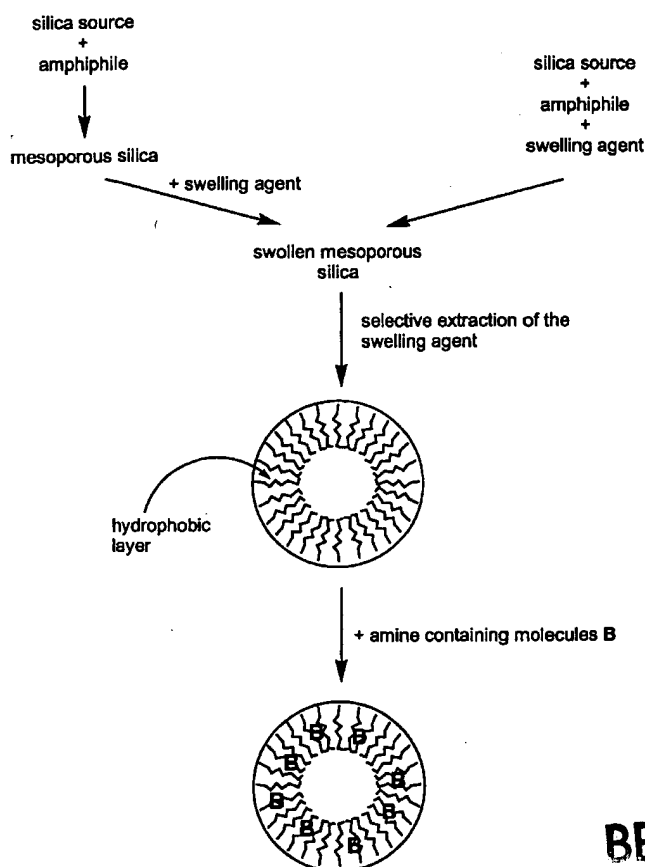
(75) Inventor/Applicant (for US only): **SAYARI, Abdelhamid**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR,  
CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,  
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,  
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,  
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU,  
SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,  
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,

[Continued on next page]

(54) Title: AMINE MODIFIED ADSORBENT, ITS PREPARATION AND USE FOR DRY SCRUBBING OF ACID GASES



(57) Abstract: The present invention provides an amine functionalised adsorbent for use in dry scrubbing process. The adsorbent comprises amine functionalised mesoporous silica in which the amine groups are present at or near the surface of the silica, including within the pore walls and channels of the silica. The present invention further provides methods of preparing the adsorbent and of using the adsorbent for the adsorption of CO<sub>2</sub> and/or other acid gases.

BEST AVAILABLE COPY

WO 2004/054708 A3



SI, SK, TR), OAPI patents (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

**(88) Date of publication of the international search report:**

14 April 2005

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J20/10 B01J20/28 B01J20/32 B01D53/40 B01D53/62 10/539225  
B01D53/047

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEAL O ET AL: "Reversible adsorption of carbon dioxide on amine surface-bonded silica gel" INORGANICA CHIMICA ACTA, vol. 240, 1995, pages 183-189, XP002298347 the whole document	1-3, 8-10,13
Y		1-3, 8-10,13, 21-24
A	US 4.999.175 A (VANSANT ETIENNE ET AL) 12 March 1991 (1991-03-12) column 1, lines 44-61 column 3, lines 9-18 column 6, lines 7-43 examples 1-3,5-16 ----- -/--	1,8,9, 21-24

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

28 September 2004

Date of mailing of the international search report

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized Officer

Goebel, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CHEMABS [Online]            CHEMICAL ABSTRACTS SERVICE, COLUMBUS,            OHIO, US;            BURWELL, ROBERT L., JR. ET AL: "Modified            silica gels as selective adsorbents for            sulfur dioxide"            XP002298351            retrieved from STN            Database accession no. 1974:496627            abstract            &amp; JOURNAL OF THE CHEMICAL            SOCIETY, CHEMICAL COMMUNICATIONS            ( 1974 ), (9), 342-3 CODEN: JCCCAT; ISSN:            0022-4936, 1974,</p>	1-3, 8-10,13
Y	<p>US 5 876 488 A (NALETTE TIMOTHY A ET AL)            2 March 1999 (1999-03-02)            cited in the application            the whole document</p>	1-3,6, 8-11,13, 21-24
Y	<p>US 2 818 323 A (VLADIMIR HAENSEL)            31 December 1957 (1957-12-31)              the whole document</p>	1-3,6, 8-10,13, 21-24
Y	<p>US 5 840 271 A (CORDOVA JOSE RAFAEL ET            AL) 24 November 1998 (1998-11-24)              column 5, lines 51-67            column 6, lines 35-46            claims 1,8,9,13; example 1</p>	1-3, 8-10,13, 21-24
Y	<p>DE 100 62 558 A (DEGUSSA)            11 July 2002 (2002-07-11)              paragraphs [0049] - [0052]            paragraph [0056]            paragraph [0058]            claims; examples</p>	1-3, 8-10,13, 21-24
X	<p>DE 100 21 165 A (HENKEL KGAA)            8 November 2001 (2001-11-08)            paragraphs [0163] - [0165]</p>	1-4,8,14
X	<p>DATABASE WPI            Section Ch, Week 200332            Derwent Publications Ltd., London, GB;            Class D15, AN 2003-338786            XP002298352            &amp; KR 2002 007 772 A (LEE J H)            29 January 2002 (2002-01-29)            abstract</p>	1-4,8,14

-/--

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 251 280 B1 (DAI SHENG ET AL) 26 June 2001 (2001-06-26) column 4, line 62 - column 5, line 2 column 7, lines 9-11 column 8, lines 4-8 examples 1-7 claims 1,9,14,24-26,33,49,50; figures 1,3,4	1-3,8,13
X	----- STEIN A ET AL: "HYBRID INORGANIC-ORGANIC MESOPOROUS SILICATES-NANOSCOPIC REACTORS COMING OF AGE" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 12, no. 19, 2 October 2000 (2000-10-02), pages 1403-1419, XP000966751 ISSN: 0935-9648 cited in the application page 1405 - page 1414 figures 1-4,6 table 1	1-5,8, 13,14
Y	-----	6,9-11, 21-24
X	PRICE ET AL: "Modified Silicas for clean Technology" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, CHEMICAL SOCIETY. LETCHWORTH, GB, 2000, pages 101-110, XP002183039 ISSN: 1472-7773 page 103; Schemes 4-6	1-3,8,13
Y	-----	14
X	CLARK ET AL: "Catalysis of liquid phase organic reactions using chemically modified mesoporous inorganic solids" CHEMICAL COMMUNICATIONS - CHEMCOM, ROYAL SOCIETY OF CHEMISTRY, GB, 1998, pages 853-860, XP002183040 ISSN: 1359-7345 pages 853-854	1-3,8,13
Y	----- -/--	14

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MACQUARRIE D J: "Organically modified hexagonal mesoporous silicas - Clean synthesis of catalysts and the effect of high loading and non-catalytic second groups on catalytic activity of amine-derivatised materials" GREEN CHEMISTRY, vol. 1, no. 4, 6 September 1999 (1999-09-06), pages 195-198, XP002298348 the whole document	1-5,8,14
Y		6,9-11, 21-24
X	----- HALL S R ET AL: "Template-directed synthesis of bi-functionalized organo-MCM-41 and phenyl-MCM-48 silica mesophases" CHEMICAL COMMUNICATIONS, no. 2, 1999, pages 201-202, XP002298349 CAMBRIDGE, UK the whole document	1-5,8,14
X	----- FOWLER C E ET AL: "Synthesis and characterization of ordered organo-silica-surfactant mesophases with functionalized MCM-type architecture" CHEMICAL COMMUNICATIONS, no. 18, 1997, pages 1769-1770, XP002298350 CAMBRIDGE UK the whole document -----	1-3,8,14

# INTERNATIONAL SEARCH REPORT

PCT/CA 03/01968

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1 (part); 2-3; 4-6, 8 (part); 9 (part); 10; 11 (part); 13-14; 21-24 (part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 (part); 2-3; 4-6, 8 (part); 9 (part); 10; 11 (part); 13-14; 21-24 (part)

insofar as relating to a composition (I) suitable for use as water-tolerant, regenerable adsorbent for use in an acid gas dry-scrubbing process, comprising surface or framework amine-functionalised mesoporous silica ("MS") or organosilica ("MOS"), such that primary, secondary or tertiary amino groups are present and wherein (I-a-1) the amine containing molecules are **\*\*covalently bonded\*\*** to the **\*\*surface\*\*** of the pore walls; processes (II-1) or (II-2) for the preparation of (I-a-1), comprising introducing the amino functionalisation by **\*\*direct grafting\*\*** or **\*\*direct co-condensation\*\*** with the help of an amphiphile molecule ("AM"); a method of dry scrubbing using (I-a-1); a two or more bed system (IV-a-1) for dry scrubbing comprising (I-a-1).

---

2. claim: 15

relating to a process (II-3) for the preparation of (I-a-1), comprising introducing the amino functionalisation by **\*\*first grafting a reactive group-containing silane\*\***, and subsequently treating the resulting product with an amine.

---

3. claim: 16

relating to a process (II-4) for the preparation of (I-a-1), comprising introducing the amino functionalisation by **\*\*co-condensation\*\*** using a reactive group-containing silane as amine precursor and subsequently treating the resulting product with an amine.

---

4. claims: 1 (part); 4-6, 8 (part); 9 (part); 11 (part); 17, 19; 21-24 (part)

insofar as relating to a composition (I), wherein (I-a-2) the pore walls have a **\*\*hydrophobic surface\*\*** and the **\*\*amine-containing molecules are dispersed within\*\*** the hydrophobic surface; processes (II-5) or (II-7) for the preparation of (I-a-2) by **\*\*either\*\*** first preparing a MS or MOS in the presence of a **\*\*swelling agent\*\*** and **\*\*selectively extracting\*\*** the swelling agent to produce a hydrophobic layer on the surface of the MS or MOS and then treating the product with an amine **\*\*or\*\*** by reacting a source of silica with an AM and simultaneously or subsequently adding an **\*\*amine containing swelling agent\*\***; a method of dry scrubbing using (I-a-2); a two or more bed system (IV-a-2) for dry scrubbing comprising (I-a-2).



FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

---

5. claims: 1 (part); 8 (part); 9 (part); 18; 21-24 (part)

insofar as relating to a composition (I), wherein (I-a) the surface is amine-functionalized by adsorbed amine molecules, \*\*excluding the subject-matter of invention group 4\*\*; a process (II-6) for the preparation of (I-a) comprising mixing a source of (organo-)silica with an \*\*AM having at least one amino group\*\* under conditions that facilitate self-assembly to produce (I-a), wherein the amine-functionalised MS or MOS has its \*\*pores filled with amine-containing AM\*\*; a method of dry scrubbing using (I-a); a two or more bed system (IV-a) for dry scrubbing comprising (I-a).

---

6. claims: 1 (part); 7; 8 (part); 9 (part); 12, 20; 21-24 (part)

insofar as relating to a composition (I), wherein (I-b) the \*\*framework is amine-functionalised\*\*; a process (II-8) for the preparation of (I-b) comprising mixing a source of \*\*organosilica\*\* with an AM to produce a MOS having a framework comprising reactive sites and subsequently \*\*introducing amino groups\*\* at the reactive sites; a method of dry scrubbing using (I-b); a two or more bed system (IV-b) for dry scrubbing comprising (I-b).

---

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4999175		12-03-1991	EP 0189606 A1	06-08-1986
			AT 45302 T	15-08-1989
			CA 1275291 C	16-10-1990
			DE 3572129 D1	14-09-1989
			JP 1049531 B	25-10-1989
			JP 1564169 C	12-06-1990
			JP 61287418 A	17-12-1986
US 5876488	A	02-03-1999	EP 0892675 A1	27-01-1999
			JP 2000502289 T	29-02-2000
			WO 9817388 A1	30-04-1998
US 2818323	A	31-12-1957	NONE	
US 5840271	A	24-11-1998	DE 19704875 A1	14-08-1997
			FR 2744933 A1	22-08-1997
			GB 2309967 A ,B	13-08-1997
			GB 2341853 A ,B	29-03-2000
			JP 3139740 B2	05-03-2001
			JP 10007474 A	13-01-1998
			NL 1005203 C2	10-08-2000
			NL 1005203 A1	12-08-1997
			US 6106802 A	22-08-2000
			US 6299855 B1	09-10-2001
			BR 9700936 A	01-09-1998
DE 10062558	A	11-07-2002	DE 10062558 A1	11-07-2002
DE 10021165	A	08-11-2001	DE 10021165 A1	08-11-2001
			AU 6386801 A	12-11-2001
			WO 0183398 A2	08-11-2001
KR 2002007772	A	29-01-2002	NONE	
US 6251280	B1	26-06-2001	NONE	